U. S. DEPARTMENT OF AGRICULTURE.

FARMERS' BULLETIN No. 146.

INSECTICIDES AND FUNGICIDES:

CHEMICAL COMPOSITION AND EFFECTIVENESS OF CERTAIN PREPARATIONS.

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LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF CHEMISTRY,
Washington, D. C., November 12, 1901.

SIR: The use of insecticides and fungicides has become almost indispensable to the farmer and fruit grower throughout the whole country. Immense quantities of these bodies are manufactured and placed upon the market, and without doubt the greater part of them meet the claims of the manufacturers. There are some instances, however, on record where the materials which are sold are not of sufficiently high standard to warrant their purchase, and to this extent commerce in them is to be discouraged.

This Bureau has undertaken, in connection with the Division of Entomology, a somewhat elaborate study of the insecticides found in the American markets. The object has been to obtain, if possible, samples of every kind of insecticide and fungicide offered for sale. The detailed chemical study of these bodies does not interest particularly the farmer and horticulturist, and the publication of matters of this kind, except a statement of the chemical composition of the samples examined, will be left for a more technical bulletin. There are many points, however, which have come out in the work which seem to be of great public interest and to merit publication in the form of a popular bulletin. It is with this view that the data which follow are offered to the public. There is no purpose in our work to interfere with a legitimate business, but it seems only proper that merchants, as well as purchasers, be acquainted with the real character of the goods in which they deal. It is probable that many of the manufacturers of so-called insecticides and fungicides are themselves not aware of the poor quality, sometimes almost uselessness, of the materials which they offer for sale. Information which will be beneficial both to the manufacturer and user of these articles will prove valuable.

The investigation has been confided to Mr. J. K. Haywood, who has prepared the bulletin now offered, the publication of which as a Farmers' Bulletin is respectfully recommended.

Very respectfully,

H. W. WILEY, *Chief of Bureau.*

Hon. JAMES WILSON,
Secretary.

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INSECTICIDES AND FUNGICIDES: CHEMICAL COMPOSITION AND EFFECTIVENESS.

PARIS GREEN.

Among the most important insecticides now on the market is Paris green, and this article deserves first consideration. Paris green, if perfectly pure chemically, is a compound made up of three substances—arsenious acid, acetic acid, and oxide of copper—joined to each other in a chemical combination called copper aceto-arsenite. These should be present in the following proportions:

	Per cent.
Arsenious acid	58.65
Copper oxide	31.29
Acetic acid	10.06

Use of arsenious acid in free state.—Because of faulty methods of manufacture, however, and also because arsenious acid is cheaper than the other constituents of Paris green, large amounts of this substance are sometimes present in the Paris green on the market not combined as it should be with the other two constituents, but present in the free state. A sample of this kind will cause great damage to the foliage by scorching, and the avoidance of such Paris green can not be too strongly recommended. The maximum amount of free arsenious acid that should be allowed in Paris green has been found in California to be 4 per cent and in Idaho between 4 and 5 per cent.

There is no easy test by which one who is not a chemist can recognize the presence of free arsenious acid in Paris green. Intending purchasers should consult bulletins on the subject which give the names of the various manufacturers, along with an analysis showing how much of the arsenious acid is free and how much combined, as it should be with the other constituents.

Addition of calcium sulphate.—Another method of adulterating Paris green is by the addition of calcium sulphate (gypsum). It is hardly necessary to state that this substance is absolutely worthless as an insecticide and is only added to give weight. Such an adulteration as this is more rare than that first mentioned, and is also much easier of detection. To apply the test for this form of adulteration take

about as much Paris green as can be held on a 5-cent piece, transfer to a drinking glass and add about six tablespoonfuls of household ammonia; stir all the time and continue stirring for about five minutes. If the green is pure a dark blue solution will be formed and no residue will remain undissolved. If calcium sulphate is present, however, a white residue will remain suspended in the blue liquid, which will soon sink to the bottom of the glass in a compact mass.

Presence of Glauber salts.—There is one other substance that commercial samples of Paris green always contain because of their method of manufacture. This is sodium sulphate (Glauber salts). This substance will neither harm nor help plants or insects. It should not be present in good samples of Paris green except in very small amounts, 1 to 1.5 per cent, since it only adds weight and causes purchasers to pay the market price of standard goods for a weaker article.

The author has recently examined 47 samples of Paris green collected by the Division of Entomology, and finds that the total arsenious acid varies from 56.2 to 62.16 per cent, the copper oxide from 27.58 to 31.16 per cent, and the acetic acid from 6.5 to 12 per cent. Out of these 47 samples 10 had more than 1.5 per cent sodium sulphate, one reaching even to 3.59 per cent. As to free arsenious acid, there are two methods for its determination: The first, or sodium acetate extraction method, shows more nearly the amount of free arsenious acid present in the original green, while the second, or water extraction method, shows the amount of free arsenious acid originally present in the green, together with some that has been set free by the action of water on the green. Although it has not yet been proved, the second method more than likely shows more accurately the value of Paris green in actual orchard practice. By extracting with sodium acetate, one sample contained 8.91 per cent and one sample 6.37 per cent. Besides these there were 2 samples containing between 3 and 4 per cent, no samples containing between 2 and 3 per cent, and the remainder containing less than 2 per cent. By extracting with water, 19 samples contained above 5 per cent free arsenious acid, 16 between 4 and 5 per cent, and the remaining 12 below 4 per cent.

There are two other substances now being sold that are very closely allied to Paris green, and consequently will be taken up in this connection.

"GREEN ARSENOID."

The first of these is "Green Arsenoid." This compound is very much like Paris green in its composition and effect on insects. If pure, it should be composed of arsenious acid and oxide of copper joined to one another in a chemical combination called copper arsenite, but unlike Paris green it does not contain any acetic acid. An analysis

of this substance shows that besides combined arsenious acid and oxide of copper it contains—

	Per cent.
Free arsenious acid (when extracted with sodium acetate)	3.23
Free arsenious acid (when extracted with cold water)	5.88
Sodium sulphate	2.02
Sand	1.30

It will at once be seen that the percentage of free arsenious acid is somewhat too high when a water extraction is used. The amount of sodium sulphate and sand present also is too large, causing the manufacturers to gain the price of over 3 pounds of Paris green on each 100 pounds sold, with an equal loss to the consumer if the price is maintained. We would not, of course, expect to have commercial articles entirely free of these two substances, but with care the sodium sulphate could easily be reduced to 1 per cent, and the sand to much less than 1 per cent. As a whole, however, this is a very good compound and has given excellent results in the various State stations, especially when mixed with a little lime.

"PARAGRENE."

The second substance spoken of above is a patented article "Paragrene." This is composed of arsenious acid, oxide of copper, acetic acid, and about 27 per cent gypsum. The gypsum, of course, is of no use as an insecticide, so is in the way and only adds weight. Also 6.12 per cent of the arsenious acid is present in a soluble condition. Consequently this can not be classed as a high-grade insecticide.

LONDON PURPLE.

London purple is another of the arsenical insecticides sold in America in large quantities. This substance is prepared by boiling a purple residue from the dye industry, containing free arsenious acid, with slaked lime. In this way a compound of these two substances, called calcium arsenite, is formed. This on exposure to the air during subsequent boiling is partly converted to a closely allied compound, calcium arsenate. Since the dye residue has accumulated some dirt during the process of manufacture, sand will also be present in all samples of London purple. It will thus be seen that this substance will consist of calcium arsenite, calcium arsenate, a dye residue, and small amounts of sand and moisture. In case not enough lime is added to the dye residue or the boiling is not continued long enough, some of the arsenious acid will be present in the free condition, thus causing the foliage to be scorched.

A chemical examination of four samples, recently made by the author, shows that the moisture varied from 1.87 to 4.07 per cent, the sand from 2.46 to 3.55 per cent, the arsenious acid from 6.40 to 17.31 per

cent, the arsenic acid from 26.50 to 35.62 per cent, and the calcium oxid (lime) from 23.59 to 25.09 per cent. If the arsenious acid and arsenic acid are combined and both calculated as arsenious acid, a variation of from 37.07 to 40.12 per cent only was noted. Cold water dissolved from these samples amounts of arsenious acid varying from 1.44 to 13.49 per cent and amounts of arsenic acid varying from 7.12 to 19.56 per cent.

Since calcium arsenate and calcium arsenite are both, however, somewhat soluble in water and since water breaks up both compounds to some extent on standing in contact with them, we are not able at present to say how much of this arsenic acid and arsenious acid are in the free condition and how much combined with the lime. It is probable that plants can bear without scorching larger quantities of these soluble arsenic salts than of free arsenious acid.

LEAD ARSENATE.

Lead arsenate is prepared by the action of lead acetate on sodium arsenate, and of all the arsenicals used as insecticides is probably the most insoluble and consequently the least liable to scorch the foliage. A recent analysis of a sample of "Swift's Lead Arsenate" in this laboratory showed that it contained—

	Per cent.
Lead oxide	58.90
Arsenic acid	25.62
Organic matter	13.00

The organic portion of the substance was composed almost entirely of two sugars—dextrose and dextrin—showing that glucose sirup had been added to the lead arsenate to cause it to stick to the foliage. Practical tests with this insecticide show that its action is excellent, and that on account of its almost entire insolubility it seldom scorches the foliage.

"PINK ARSENOID."

Closely allied to lead arsenate is lead arsenite sold by one firm under the name of "Pink Arsenoid" and prepared by the action of lead acetate on sodium arsenite. This substance was found by the California Experiment Station (Bulletin 126) to consist of arsenious oxide, lead oxide, small amounts of impurities, and a small amount of a pink dye stuff to color it. Only 3.24 per cent of the arsenious acid was in the free condition. This, next to lead arsenate, is probably as insoluble as any of the arsenicals, and according to reports from various experiment stations has given good results.

"WHITE ARSENOID."

Another of the arsenites—barium arsenite—was recently put on the market under the name of "White Arsenoid." This is prepared by dissolving arsenious acid in a solution of sodium carbonate and treat-

ing the resulting fluid with barium chloride. There will be formed a compound of barium oxide and arsenious acid, barium arsenite and a compound of barium oxide and carbonic acid, barium carbonate. The results from this mixture have not been good, and a chemical analysis shows that all of the arsenious acid is dissolved by cold water; so it has, it is understood, been withdrawn from the market.

"SLUG SHOT."

There is a compound called "Slug Shot" that is very extensively sold because of its cheapness. An analysis of this substance shows that it is composed almost exclusively of crude gypsum with a small amount of arsenious acid and copper oxide added, probably in the form of Paris green. The amounts of these two substances in a sample recently examined were only 1.58 per cent arsenious oxide and 0.58 per cent copper oxide. It is needless to say that an article containing as little arsenious oxide and copper as the above will do little or no good as an insecticide, while 5 cents per pound is a large price to pay for a sample consisting of nearly 100 per cent gypsum.

"BUG DEATH."

Another insecticide that has recently come into great prominence and had a very large sale all over the United States is "Bug Death." This substance is composed largely of zinc oxide with small amounts of iron oxide and lead oxide and about 3.27 per cent of ammonium and potassium chlorides. Of course the chlorides of potassium and ammonium would be of some value as plant food as far as they go.

The Sixteenth Annual Report of the Maine Agricultural Experiment Station (1900) says in regard to this insecticide:

When it is applied to potato vines at the rate of 40 pounds to the acre it has no appreciable effect on bugs, nor does it affect the foliage.

When it is applied at the rate of 100 pounds to the acre it frees the vines of bugs, but at the same time some of the leaves curl up and die.

As a fungicide this compound is of not much value, although it has a slight effect in preventing blight when applied at the rate of 180 pounds to the acre.

Finally the following remarks are made:

Because of its high cost and slow application no one growing any considerable amount of potatoes can afford to use Bug Death. The price of the labor required to apply Bug Death to 1 acre will buy the material and spray 2 acres with Bordeaux mixture and Paris green.

"BLACK DEATH."

"Black Death" is another insecticide that is now on sale in various localities. It is composed of about—

	Per cent.
Sand and charcoal	23.00
Gypsum and limestone	75.00
Arsenious acid	.97
Copper oxide	.59

The same statements made in regard to "Slug Shot" will apply to this mixture also.

"SMITH'S VERMIN EXTERMINATOR."

This substance, advertised to kill every species of worm, bug lice, etc., and selling at the rate of 5 cents per box, is composed of partly air-slaked lime, treated with about 3 per cent crude carbolic acid and colored with a pink dye. Even if this compound contained 50 to 60 per cent instead of 3 per cent of carbolic acid, its value as an insecticide would be extremely doubtful, but as it is, it is worthless.

LICE EXTERMINATORS.

Besides the insecticides usually spoken of in agricultural bulletins, attention is called to certain others. These are the lice killers on the market, a number of which are not worth the boxes they are put up in.

"P. D. Q."—One lice and flea exterminator analyzed in this laboratory and selling at the rate of 25 cents per box, "P. D. Q.," was found to contain about 15.5 per cent sulphur, a very small amount of some volatile substance that possessed the odor of naphthalene, and other higher coal-tar products, and 80 per cent of what appeared to be only common earth.

"**Instant Louse Killer.**"—Another sample, selling at 25 cents per box, is "Instant Louse Killer." This consists of a very small amount of tobacco, a large amount of partially air-slaked lime treated with a small amount of the higher products of coal tar, and a large amount of what appears to be clay.

"**Lambert's Death to Lice.**"—Still another sample, "Lambert's Death to Lice," and selling at 25 cents per box, was analyzed. It is a mixture of tobacco with a small amount of lime, which appeared to have been treated with the higher products of coal tar. Either through negligence in cleaning the tobacco or on purpose a large amount of sand is present.

It will at once be seen that all three of these lice killers are frauds. The first, it is true, does contain sulphur and a substance like naphthalene, each of which is good in driving away vermin, but it also contains 80 per cent of worthless earth for which we are paying at the rate of 20 cents per pound. The second contains nothing that will kill vermin except tobacco, and some of the higher products of coal tar, and these are present in such small quantities as to be practically of no use. The third contains enough tobacco to perhaps be of some value, but the same amount of good tobacco as in the sample could be bought for one third as much as the cost of the "Death to Lice."

ROACH DESTROYERS.

Other preparations that are very extensively sold are the roach destroyers. These usually appear in two forms, as powders and

pastes. An analysis of a number of the powders shows that nearly all of them have borax as their chief constituent. This is sometimes mixed with meal, sometimes with flour, sometimes with sugar, sometimes with Persian insect powder, sometimes with cloves, etc. The mixture is often colored with pink or blue dye stuffs. Nearly all could be prepared at home at one-half to one-tenth the cost of the store preparations. As to the pastes, all of these have from 1 to 2 per cent of phosphorous as their poisonous principle. The remainder is sometimes molasses and corn meal or flour, and sometimes glucose sirup and corn meal or flour.

BORDEAUX MIXTURE.

Probably the most important of all fungicides is Bordeaux Mixture prepared by the action of lime suspended in water on a solution of copper sulphate (blue vitriol). It has been pointed out in Farmers' Bulletin 38 of this Department that the way of mixing these two constituents has a very appreciable effect on the chemical and physical properties of the mixture. It was further pointed out that if both solutions are dilute when mixed, a product will be formed which will stay in suspension and adhere to the foliage much better than if both solutions were concentrated. There are now several firms putting up an article called "Dry Bordeaux Mixture." This article represents an attempt to supply the ready mixed Bordeaux Mixture to the consumer, but such an attempt can hardly be successful. In the first place, drying the mixture is a step farther than using concentrated fluids, so that the dry product obtained in such a way would have very different chemical characteristics from the mixture properly prepared. Again, when we dry the mixture the suspended particles become much coarser, so that when completely dry we would have a substance the principal part of which, i. e., the oxide of copper, would hardly stay in suspension at all, but would immediately sink to the bottom.

"GRAPE DUST."

"Grape Dust" is an article put up for the treatment of diseases of the grape vine. It contains—

	Per cent.
Gypsum	35.00
Sulphur	60.00
Copper oxide	.90

And 4 per cent (about) of other indifferent substances.

Two of these constituents, i. e., sulphur and oxide of copper, are of course valuable for the purpose intended, but the 35 per cent of gypsum is of no value, and only adds weight.

"VELTHA."

"Veltha," another fungicide, contains—

	Per cent.
Sand and carbon	35
Sulphate of iron (green vitriol or copperas)	65

This latter compound of course has some value as a fungicide, but the 35 per cent of sand and carbon only add weight.

"FIBRO FERRO FEEDER."

This is another substance said to be both a fungicide and a plant food. An analysis made by the Maryland Agricultural Experiment Station (The Analysis of Commercial Fertilizers, 1893) shows that it has neither nitrogen, potash, nor phosphoric acid; so of course it is of no value as a plant food. An analysis made in this laboratory shows that it consists of quite a large amount of organic matter, chloride of iron, and sulphate of iron (green vitriol) which has been partly dehydrated and partly oxidized to ferric sulphate. Although the green vitriol is of some value as a fungicide and the chloride of iron may be of use in certain cases of plant diseases, the same amount of these two ingredients as are in the Fibro Ferro Feeder could be bought for much less, and unmixed with worthless matter.

DESIRABILITY OF ASCERTAINING COMPOSITION AND VALUE OF COMPOUNDS BEFORE PURCHASING.

In view of the fact that so many of the above insecticides and fungicides are either fraudulent or extremely expensive, considering the value of the ingredients employed, it would be well for the public to be very sure of the composition and value of any such compound before purchasing. In many cases this can be done by consulting bulletins from the local experiment stations dealing with this subject. In some States the data published concerning the composition of insecticides and fungicides is extremely meager or entirely lacking. It is to supply this want that the Bureau of Chemistry has issued this bulletin, which is somewhat of a preliminary report to a bulletin more technical in character, which is in course of preparation, giving the exact chemical composition of many of these substances, bought on the open market in nearly every State of the Union.

The Bureau of Chemistry will make analyses of samples of insecticides and fungicides purchased by farmers and others using such bodies, if instructions for securing and forwarding these samples are obtained from this Bureau.

NOTES REGARDING DEPARTMENT PUBLICATIONS.

The publications of the U. S. Department of Agriculture are mainly of three general classes:

I. Publications issued annually, comprising the Yearbooks, the Annual Reports of the Department, the Annual Reports of the Bureau of Animal Industry, and the Annual Reports of the Weather Bureau.

II. Other departmental reports, divisional bulletins, etc. Of these, each Bureau, Division, and Office has its separate series, in which the publications are numbered consecutively as issued. They comprise reports and discussions of a scientific or technical character.

III. Farmers' bulletins, divisional circulars, reprinted Yearbook articles, and other popular papers.

The publications in Class I are distributed by the Department and by Senators, Representatives and Delegates in Congress. For instance, of the 500,000 copies of the Yearbook usually issued, the Department is allotted only 30,000, while the remaining 470,000 copies are distributed by Members of Congress. The Department's supply of the publications of this class is, therefore, limited, and consequently has to be reserved almost exclusively for distribution to its own special correspondents, and in return for services rendered.

The publications of Class II are not for distribution by Members of Congress, and they are not issued in editions large enough to warrant free general distribution by the Department. The supply is used mainly for distribution to those who cooperate with the Department or render it some service, and to educational and other public institutions. A sample copy of this class of publications can usually be sent on application, but, aside from this, the Department generally finds it necessary to refer applicants to the Superintendent of Documents, of whom further mention is made below.

The publications of Class III treat in a practical way of subjects of particular interest to farmers. They are usually issued in large editions, and are for free general distribution by the Department. The Farmers' Bulletins are also for distribution by Senators, Representatives and Delegates in Congress, to each of whom is furnished annually, according to law, a quota of several thousand copies for distribution among his constituents.

A limited supply of nearly all the publications in Classes I and II is, in compliance with the law, placed in the hands of the Superintendent of Documents for sale at cost of printing. Application for these should be addressed to the **Superintendent of Documents, Union Building, Washington, D. C.,** and should be accompanied by postal money order, payable to him for the amount of the price. No postage stamps or private checks should be sent. The Superintendent of Documents is not permitted to sell more than **one copy** of any public document to the same person. The Public Printer may sell to one person any number not to exceed 250 copies if ordered before the publication goes to press.

The Secretary of Agriculture has no voice in designating the public libraries which shall be depositories of public documents. Of the distribution of documents to such depositories, including the publications of this and all other Departments of the Government, the Superintendent of Documents has full charge.

For publications of the Weather Bureau, requests and remittances should be directed to the Chief of the Weather Bureau.

The Department has no list of persons to whom all publications are sent. The Monthly List, issued on the first day of each month, will be mailed regularly to all who apply for it. The Department also issues and sends out to all who apply for them a complete list of all publications of which the Department has a supply for free distribution, and a similar list of all the Department's publications for sale by the Superintendent of Documents.

FARMERS' BULLETINS.

The following is a list of the Farmers' Bulletins available for distribution, showing the number, title, and size in pages of each. Copies will be sent to any address on application to Senators, Representatives, and Delegates in Congress, or to the Secretary of Agriculture, Washington, D. C.:

16. Leguminous Plants. Pp. 24.
19. [Superseded by No. 127.]
21. Barnyard Manure. Pp. 32.
22. The Feeding of Farm Animals. Pp. 32.
23. [Superseded by No. 142.]
24. Hog Cholera and Swine Plague. Pp. 16.
25. Peanuts: Culture and Uses. Pp. 24.
26. [Superseded by No. 129.]
27. Flax for Seed and Fiber. Pp. 16.
28. Weeds: And How to Kill Them. Pp. 32.
29. Souring and Other Changes in Milk. Pp. 23.
30. Grape Diseases on the Pacific Coast. Pp. 15.
31. Alfalfa, or Lucern. Pp. 24.
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39. Onion Culture. Pp. 31.
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135. Sorghum Sirup Manufacture. Pp. 40.
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138. Irrigation in Field and Garden. Pp. 40.
139. Emmer: A Grain for the Semiarid Regions. Pp. 16.
140. Pineapple Growing. Pp. 48.
141. Poultry Raising on the Farm. Pp. 16.
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143. The Conformation of Beef and Dairy Cattle. (In press.)
144. Experiment Station Work—XIX. (In press.)
145. Carbon Bisulphid as an Insecticide. (In press.)

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